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HYDROMETALLURGY OF ZINC ORES WITH HIGH SILICA CONTENT SOLUBLE IN ACID, PARTICULARLY THOSE OF SILICATE TYPE

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HYDROMETALLURGY OF ZINC ORES WITH HIGH SILICA CONTENT SOLUBLE IN ACID, PARTICULARLY THOSE OF SILICATE TYPE

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1. Zinc carbonate and silicate ores constitute important deposits in certain regions. Zinc silicate ores are the only ones found so far in Brazil in sufficient quantity to justify the setting up of a zinc metallurgy.

2. It is impracticable to make use of zinc silicate ores by pyrometallurgy. Their reducibility is intrinsically very low, as E. C. Truesdale and W.K. Warung demonstrate in their fundamental investigation, Relative Rates of Reactions Involved in Reduction of Zinc Ores, Metals Technology (AIME), April (1941). That is why special processes have been developed to make use of such ores, processes aiming to obtain zinc oxide and not metallic zinc, such as those of Wethrill and Waelz.

3. Such silicate ores also present a serious problem when an effort is made to use them by hydrometallurgical processes, as a result of the formation of silicic acid during their lixiviation by acids. We quote from page 16 of the work by George D. Van Arsdale, Hydrometallurgy of Base Metals, McGraw-Hill Book Co., Inc. (1953):

> "As far as is known, no ores of zinc are leached directly to recover the metal."

And again on page 17 he says:

> "Carbonate and silicate ores have yet to be handled with complete success and perhaps a leaching method will some day prove suitable for treating them."

4. Difficulties caused by formation of silicic acid during lixiviation are not exclusive of silicate ores. Many concentrates of ustulate sphalerite have a silica content, soluble in sulphuric acid, of up to 2 or 3 per cent. It may derive from silicates originally existing in the ore and not separated in the process of concentration of the sulphide or the silicates may be formed during ustulation of a concentrate containing a quartziferous gangue. In low concentrations the silicic acid greatly diminishes the speed of sedimentation of the solids in a lixiviation suspension, and markedly obstructs the pores of filtering surfaces, making necessary installations with large filtration surfaces. When the percentage of silica is higher, however, as in the case with minerals abundant in Brazil in the regions of Vazante and Januária, State of Minas Gerais, where the content of silica soluble in sulphuric acid is in the order of 10 to 25 percent of SiO_2, the suspensions obtained in lixiviation, aside from not being filtrable, form a kind of jelly which makes it impossible to recover the zinc made soluble during the leaching.

5. An example of the treatment of sulphide ores containing a small proportion of silicates soluble in acid is that of the Rhodesia-Broken Hill Development Co. In order to eliminate the solubilized silica they promote the oxidation of part of the Fe II with manganese ore and the rest with manganese bioxide from the electrolytic tanks. Then as a result of a very slow and careful neutralization, the temperature being controlled at about 70° C and kept there while the suspension is agitated, the iron precipitates in the form of iron hydroxide III and the silica is transformed into a gel of granular form. A test is then made to see if the silica is properly granulated; 250 ml of the suspension is filtered through a Buchner funnel of 10 cm diameter, and the filtration time is noted until the cake shows cracks. If the filtration time is less than 8 minutes the suspension is considered properly granulated; if longer, agitation is continued until the filtration test comes out satisfactorily.

6. When lixiviation is carried out on zinc ores containing 58.4% of ZnO and 24.7% of SiO_2 (95% of silica content being soluble in sulphuric acid at 100 g/l), use of the above-described technique for elimination of silica provides suspensions that require at least 1.5 hours for filtration of 250 ml. The time is excessively long; and it takes about 4 hours to filter the same volume when the Fe III ion is not used to coagulate the silica.

7. Assuming that the silicic acid formed in the lixiviation is in the form of a colloid solution with the particles negatively charged, we gave thought to the use of ions other than iron which would show a high flocculating power, whose sulphurates would be soluble in heated solutions of zinc sulphate without decomposition or hydrolysis, and which could easily be obtained industrially at low cost. Aluminum being the element most nearly meeting these conditions, we decided to use it in our experiments.

8. We found that the use of quantities of aluminum sulphate in the proportion of 7 to 10.5 per cent of Al_2O_3 in relation to the soluble silica of the ore, and by attacking the said ore with solutions of sulphuric acid at 50 g/l, extraordinarily rapid filtrations were obtained, although the volumes of the filtration cakes were relatively large on the order of 5 kg of moist cake for each kg of zinc ore. The filtration times of the samples, under conditions as described in paragraph 6, were under 2 minutes.

9. The inconvenience caused by the large volume of the cake was removed by adoption of a new technique in leaching the ore. It was found experimentally that, upon addition of sulphuric acid solution to a lixiviated suspension already totally neutralized in which the silica was already coagulated, an appreciable sedimentation of the solids in the suspension was obtained. The filtration cake was quite reduced in volume, although the filtration time was relatively long when an acid filtration medium was used. We also observed that the silica already coagulated did not again enter into solution.

10. Proceeding from this observation we finally developed a new technique of lixiviation. We now acidulated a lixiviated suspension, already neutralized, with a charge of sulphuric acid solution equal to that used in the first lixiviation, and later neutralized this charge of acid with an equivalent charge of ore. A charge of acid was again poured over the suspension thus obtained, and this charge then neutralized with another of ore. Half an hour was allowed to pass between successive additions of acid or ore. Before carrying out the fourth addition of acid in the lixiviation tank, a third of the volume of lixiviated suspension was removed and sent on for filtration. We continued in this way in the same sequence with alternate additions of acid and ore, and before each addition of acid we took out a third of the volume of the lixiviated suspension in the tank. With each charge of acid there was added, simultaneously, a certain quantity of aluminum sulphate.

11. A number of interesting facts were observed. The suspension became more fluid, although there was little change in fluidity from the fourth charge on. Sedimentation was progressively greater and faster as the number of operations increased, and was stabilized from the eighth on. The volume of precipitate diminished with the sequence of operations, tending toward a minimum limit depending on the quantity of aluminum sulphate used and also being somewhat influenced by the temperature; it varied around 1.5 kg of moist cake per kg of ore. Retention of soluble zinc in the filtration cakes was very low when the cakes were washed with displacements on the order of 150 to 200 per cent. With each addition of acid the aluminum already precipitated in a previous operation again entered into solution in a proportion of 60%; this of course made it possible to reduce the quantity of aluminum sulphate necessary to maintain a given speed of filtration and weight of the cake.

12. The factory which is being built in the municipio of Itaguai, state of Rio de Janeiro, with financing by the National Bank of Economic Development, for zinc metallurgy by the hydrometallurgical process, is based on the lixiviation technique described above. The said process has been tested in a pilot plant that has been in operation for almost five years, producing 200 kg of zinc per day using calamine from Vazante and willemite from Januária. The recovery of soluble zinc contained in the filtration cake has been on the average above 96%, with a washing displacement on the order of 150 to 200% and a filtering surface of 1 m^2 per ton of zinc per day. The new lixiviation technique has been used, but conventional processes have been used for the subsequent purification of the solution of zinc sulphate obtained, before proceeding to its electrolysis.

13. Once the scientific solution had been found in the laboratory, a pilot plant was set up to test whether the new invention was practicable as well as economically sound.

14. Once the results obtained in the laboratory were confirmed and the viability of the new production process demonstrated in practice, it was decided that the zinc plant should have a daily capacity of 20 tons, that is, 7200 tons annually of zinc in ingots.

15. During the phase of installation, construction of the plant will have a substantial impact on the economy of the Guanabara-State of Rio de Janeiro region, since the project will be largely based on local factors. A certain amount of machinery must be imported from São Paulo, but nothing from abroad.

16. As to the impact of the undertaking when it goes into operation, some of its beneficial effects on the regional and national economy are given below. As regards the regional economy, account should be taken of the economy of the Guanabara-State of Rio de Janeiro region and of the economy of the region which the zinc ore will come from.

17. As to the first region - where the plant is located - the following effects may be listed:

i) Use of unskilled labour from the rural sector - 65 labourers - with consequent improvement of their living standards because of higher wages and greater productivity; 41 skilled workers will also be used.

ii) Benefits to the finances of the Município of Itaguai because of increased receipts from taxes applying to the new industry, and indirectly through development of other activities.

iii) Increase of state revenues, in the amount of Cr$ 86.400 thousand per year through collection of the Tax on Sales and Consignments and the Electrification Fund. This does not include the revenue derived from increased commercial transactions resulting from increased demand for goods of immediate consumption; this will be equivalent to the greater part of the annual payroll (Cr$ 60 million).

18. As to the second region mentioned above - the municípios of Vazante and Januária - the benefits indicated can be extended to include the establishment there of mining activity on a definitive and continuous basis. The socio-economic effects will be of major significance, as this is one of the most underdeveloped regions in the country; even farming and cattle-raising have not yet succeeded in gaining a systematic foothold there on account of bad climate, irregular rains and low soil fertility.

19. If this zinc ore is made use of - it never has been and certainly never would be were it not for the technical innovation adopted - it will represent a flow into the said region of some Cr$ 30 million annually, an amount corresponding to the wages to be paid to workers in the mines.

20. As to the impact on the national economy as a whole, aside from the direct effect on income (an additional net value of Cr$ 800 million a year) and its reflex effects on the regional economies as already indicated, the following facts should also be considered:

i) Increase of federal revenue through Income Tax and Additonal Income Tax; the amount will be approximately Cr$ 150 million annually.

ii) Training in advance of the workers recruited for the plant, thus improving national know-how without spending a single unit of exchange and without importing technicians.

iii) By virtue of having carried out research, experimentation and investment to discover the new production process, the plant has contributed to increase the stimulus to the small class of Brazilian scientists, and has also given publicity abroad to our inventive and technical capacity.

iv) Use of national mineral resources: zinc ore 24,000, bauxite 396, manganese ore 230 and limestone 180 tons/year.

v) The factory by production of zinc in ingots will provide Brazil with a net annual saving in exchange, on the average, of approximately 2 million dollars.

21. Just as all the raw materials to be used for production of this metal are of domestic origin, so all equipment and installations will be acquired in Brazil.

22. Consequently, the project that is being carried out represents a promising milestone on the road to Brazilian economic development. We are pleased to point out that the whole project, from the conception and research to develop the new productive process to the technical specifications and designs of special equipment, has been under the charge of Brazilian technicians.

23. In addition to marking the beginning of zinc metallurgy in Brazil, the project also demonstrates the flowering in this country of a new attitude in approaching scientific research and technical problems, thus contributing to the beginning of a process of replacing imported know-how.

24. The apparent average consumption of zinc in ingots in Brazil for the 3-year period 1958/60 was 25,412 tons. Consumption tends to expand rapidly, as seen by the fact that in the 3-year period 1948/50, only 10 years earlier, the annual average was no more than 8550 tons. It is to be expected that demand for zinc will continue to increase in the coming years, perhaps at an even faster rate than in the past, in virtue of the accelerated rate of national development.

25. It is estimated that in 1963, when the plant is scheduled to begin production, the demand for zinc in ingots in the Brazilian market will come close to 35 thousand tons a year. It is thus clear that the project has ample possibilities of success, since it can count from the first on a market 5 times as great as the production planned for the initial period.

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